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Abstract of JP2000309775

PROBLEM TO BE SOLVED: To obtain a phosphor having a high afterglow luminance and a long afterglow time by forming a phosphorescent phosphor having a specific Eu- activated or Pb-activated structure. **SOLUTION:** The Eu-activated phosphorescent phosphor is represented by the formula: MO.aSiO₂.bR₂O.cX.dM'2O₃; EuyLnz, is efficiently excited by the irradiation with visible light or an ultraviolet ray of 254 nm and has a luminescent peak at a wavelength of 530 nm or higher and a luminescent peak at a wavelength of 440-530 nm, The Pb-activated phosphorescent phosphor is represented by the formula: MO.aSiO₂.bR₂OcX.dM'2O₃; PbyLnz, is excited by the irradiation with an ultraviolet ray of 254 nm and has the maximum peak at a wavelength of 440 nm or lower, In the formulas, M is Ba, Sr, Ca, Mg or Zn; R is Li, Na or K; X is F, Cl, Br or I; M' is B or Al; the coactivator Ln is Sc, Y, La, Ce, Pr, Nd, Ti, Zr, Hf or the like; 0<=a<=0.4; 0<=b<=0.1; 0<=c<=0.1; 0<=d<=0.1; 0.00001<=y<=0.1; and 0<=z<=0.3.

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(54)【発明の名称】 蓄光性蛍光体

(57)【要約】

【課題】 残光輝度が高く、残光時間が長い、また、励起波長を変えることによって多様な残光色が得られる、新規酸化物系蓄光性蛍光体を提供する。

【解決手段】 EuまたはPbで賦活された蓄光性蛍光体であり、その化学組成式が $MO \cdot aSiO_2 \cdot bR_2O \cdot cX \cdot dM'_{2}O_3 : (Eu, Pb), Ln_2$ (ただし、MはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる1種または2種以上であり、RはLi, Na, Kのアルカリ金属イオンからなる群から選ばれる少なくとも1種以上であり、XはF, Cl, Br, Iからなる群から選ばれる少なくとも1種以上であり、M'はBまたはAlであり、共賦活剤LnはNd, Dy, Tm, Mn, Biの中から選ばれる少なくとも1種以上である。)で示される。

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【特許請求の範囲】

【請求項1】 Euで賦活された蓄光性蛍光体であり、その化学組成式が $MO \cdot aSiO_4 \cdot bR_2O \cdot cX \cdot dM'_2O_4 : Eu, Ln$ 。(ただし、MはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる1種または2種以上であり、RはLi, Na, Kのアルカリ金属イオンからなる群から選ばれる少なくとも1種以上であり、XはF, Cl, Br, Iからなる群から選ばれる少なくとも1種以上であり、M'はBまたはAlであり、共賦活剤LnはSc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, Wの中から選ばれる少なくとも1種以上である。)で示され、a, b, c, d, y, zはそれぞれ $0 \leq a \leq 0.4$, $0 \leq b \leq 0.1$, $0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$, $0.00001 \leq y \leq 0.1$, $0 \leq z \leq 0.3$ の範囲にある蓄光性蛍光体。

【請求項2】 aが、 $0 < a \leq 0.4$ の範囲にある請求項1に記載の蓄光性蛍光体。

【請求項3】 前記の共賦活剤LnがNd, Dy, Tm, Mn, Biの中から選ばれる少なくとも1種以上である請求項1又は2記載の蓄光性蛍光体。

【請求項4】 bが、 $0.00001 < b \leq 0.1$ の範囲にある請求項1から3のうちいずれか一項記載の蓄光性蛍光体。

【請求項5】 cが、 $0.00001 < c \leq 0.1$ の範囲にある請求項1から4のうちいずれか一項記載の蓄光性蛍光体。

【請求項6】 dが、 $0.00001 < d \leq 0.1$ の範囲にある請求項1から5のうちいずれか一項記載の蓄光性蛍光体。

【請求項7】 254nmの紫外線を照射した後の発光スペクトルにおいて、530nmを超える波長の発光ピークを有する請求項1から6のうちいずれか一項記載の蓄光性蛍光体。

【請求項8】 可視光を照射した後の発光スペクトルにおいて、530nmを超える波長の発光ピークを有する請求項1から7のうちいずれか一項記載の蓄光性蛍光体。

【請求項9】 可視光を照射した後の発光スペクトルにおいて、530nmを超える波長の発光ピークを有することに加えて、440nmを超えて530nm以下の範囲に少なくとももう一つ以上の発光ピークを有する、請求項8記載の蓄光性蛍光体。

【請求項10】 可視光を照射した後の発光スペクトルにおいて、530nmを超える波長の発光ピークを有することに加えて、440nmを超えて530nm以下の範囲に少なくとももう一つ以上の発光ピークを有する蓄光性蛍光体であって、530nmを超える発光ピーク波

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長の励起スペクトルにおいて400nmを越えて450nm以下の範囲に最大励起波長を有し、かつ、440nmを超えて530nm以下の発光ピーク波長の励起スペクトルにおいて300nm以上400nm以下の範囲に最大励起波長を有する蓄光性蛍光体。

【請求項11】 Pbで賦活された蓄光性蛍光体であり、その化学組成式が $MO \cdot aSiO_4 \cdot bR_2O \cdot cX \cdot dM'_2O_4 : Pb, Ln$ 。(ただし、MはBa, Sr, Ca, Mg等のアルカリ土類金属およびZnからなる群から選ばれる1種または2種以上であり、RはLi, Na, Kのアルカリ金属イオンからなる群から選ばれる少なくとも1種以上であり、XはF, Cl, Br, Iからなる群から選ばれる少なくとも1種以上であり、M'はBまたはAlであり、共賦活剤LnはSc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, Wの中から選ばれる少なくとも1種以上である。)で示され、a, b, c, d, y, zはそれぞれ $0 \leq a \leq 0.4$, $0 \leq b \leq 0.1$, $0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$, $0.00001 \leq y \leq 0.1$, $0 \leq z \leq 0.3$ の範囲にある蓄光性蛍光体。

【請求項12】 254nmの紫外線を照射した後の発光スペクトルにおいて、440nm以下の波長の最大発光ピークを有する請求項1記載の蓄光性蛍光体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、アルカリ土類金属またはZnの酸化物を含み、EuまたはPbで賦活された蓄光性蛍光体に関するものである。

【0002】

【従来の技術】 蛍光とは、物質が外部からの刺激(励起)によって可視域付近の光を発する現象であり、蛍光灯、放電ランプ、CRT(Cathode Ray Tube)いわゆるブラウン管などの発光がこれにあたる。蛍光を発する物質を蛍光体というが、励起停止後に目に感じられる程度の時間(0.1s程度)の蛍光が続く場合を残光と呼ぶ。そして残光時間が室温で数時間に及ぶような長残光性を持つ蛍光体を、蓄光性蛍光体と呼んでいる。

【0003】 このような蓄光性蛍光体としては、昔からZnS:Cu(黄緑色発光), CaSrS:Bi(青色発光), ZnCdS:Cu(オレンジ色発光), CaS:Bi(紫色発光)などの硫化物系が知られている。化学耐久性が非常に悪かったり、Cdのような有毒なものを含んだりするため、実際に現在実用化されたのはZnS:Cuのみであるが、残光時間がせいぜい3時間程度で短いという問題点があり、さらに日光に含まれる紫外線ならびに大気中の水分により、ZnS + H₂O → Zn + H₂Sの形に分解されて粒子自体が黒化し、短期間

で残光輝度が著しく低下するという致命的欠点を有している。そのため、この蓄光体は主に夜光時計や屋内の夜間表示など非常に限られた用途に限定されていた。

【0004】最近、酸化物でも蓄光性蛍光体が見いだされている。例えば、 $m(S_{r...}Eu_{x})O \cdot nA_{1..}O \cdot yB_{2}O$ 系(中国特許:CN1053807A)、 $M_{1..}A_{1..}O_{4..} : Eu$ 、 Dy 系(特開平8-127772)、 $m(S_{r...}M^{3..})O \cdot n(Mg_{1..}M^{3..})O \cdot 2(S_{i...}Ge_{..})O_{2..} : Eu Dy$ 系が報告されている。

これらの材料は残光輝度と残光時間が共に上述の硫化物系に比べて大幅に向上了ので、より幅広い用途が期待される。しかし、いずれの系においても最大発光ピーク波長が440nmを越え、530nm以下の範囲にあり、530nmを越える波長の発光ピークを有するものや、440nm以下の波長の最大発光ピークを有するものはないのが現状である。

【0005】

【発明が解決しようとする課題】本発明は、上記従来技術の問題点を解決し、残光輝度が高く残光時間が長い、新規酸化物系蓄光性蛍光体を提供することを課題とする。

【0006】

【課題を解決するための手段】本発明者は、これまでに知られていないホスト組成に希土類元素やPbなどを添加し鋭意試験研究を行った結果、Euで賦活して、254nmの紫外線を照射した後の発光スペクトルにおいて530nmを越える波長の発光ピークを有する蓄光性蛍光体を見いだし、また、Pbで賦活して、440nm以下の波長の最大発光ピークを有する蓄光性蛍光体を見いだし、本発明をなすに至った。

【0007】すなわち、請求項1に記載の発明は、Euで賦活された蓄光性蛍光体であり、その化学組成式が $M_{1..}O \cdot aS_{i..}O_{2..} \cdot bR_{2..}O \cdot cX \cdot dM'_{2..}O_{3..} : Eu, L_{n..}$ (ただし、MはBa、Sr、Ca、Mg等のアルカリ土類金属およびZnからなる群から選ばれる1種または2種以上であり、RはLi、Na、Kのアルカリ金属イオンからなる群から選ばれる少なくとも1種以上であり、XはF、Cl、Br、Iからなる群から選ばれる少なくとも1種以上であり、M'はBまたはA1であり、共賦活剤LnはSc、Y、La、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb、Lu、Cr、Mn、Bi、Sn、In、Sb、As、Ti、Zr、Hf、P、Nb、Ta、V、Mo、Wの中から選ばれる少なくとも1種以上である。)で示され、a、b、c、d、y、zはそれぞれ $0 \leq a \leq 0.4$ 、 $0 \leq b \leq 0.1$ 、 $0 \leq c \leq 0.1$ 、 $0 \leq d \leq 0.1$ 、 $0 \leq 0.0001 \leq y \leq 0.1$ 、 $0 \leq z \leq 0.3$ の範囲にある蓄光性蛍光体である。

【0008】また、請求項2に記載の発明は、aが、 $0 < a \leq 0.4$ の範囲にある請求項1に記載の蓄光性蛍光

体であり、請求項3に記載の発明は、前記の共賦活剤LnがNd、Dy、Tm、Mn、Biの中から選ばれる少なくとも1種以上である請求項1又は2記載の蓄光性蛍光体であり、請求項4に記載の発明は、bが、 $0.0001 < b \leq 0.1$ の範囲にある請求項1から3のうちいずれか一項記載の蓄光性蛍光体であり、請求項5に記載の発明は、cが、 $0.000001 < c \leq 0.1$ の範囲にある請求項1から4のうちいずれか一項記載の蓄光性蛍光体であり、請求項6に記載の発明は、dが、 $0.0001 < d \leq 0.1$ の範囲にある請求項1から5のうちいずれか一項記載の蓄光性蛍光体であり、請求項7に記載の発明は、254nmの紫外線を照射した後の発光スペクトルにおいて、530nmを越える波長の発光ピークを有する請求項1から6のうちいずれか一項記載の蓄光性蛍光体である。

【0009】また、請求項8に記載の発明は、可視光を照射した後の発光スペクトルにおいて、530nmを越える波長の発光ピークを有する請求項1から7のうちいずれか一項記載の蓄光性蛍光体であり、請求項9に記載の発明は、可視光を照射した後の発光スペクトルにおいて、530nmを越える波長の発光ピークを有することに加えて、440nmを越えて530nm以下の範囲に少なくとももう一つ以上の発光ピークを有する、請求項8記載の蓄光性蛍光体である。

【0010】また、請求項10に記載の発明は、可視光を照射した後の発光スペクトルにおいて、530nmを越える波長の発光ピークを有することに加えて、440nmを越えて530nm以下の範囲に少なくとももう一つ以上の発光ピークを有する蓄光性蛍光体であって、530nmを越える発光ピーク波長の励起スペクトルにおいて400nmを越えて450nm以下の範囲に最大励起波長を有し、かつ、440nmを越えて530nm以下の発光ピーク波長の励起スペクトルにおいて300nm以上400nm以下の範囲に最大励起波長を有する蓄光性蛍光体である。

【0011】また、請求項11に記載の発明は、Pbで賦活された蓄光性蛍光体であり、その化学組成式が $M_{1..}O \cdot aS_{i..}O_{2..} \cdot bR_{2..}O \cdot cX \cdot dM'_{2..}O_{3..} : Pb, L_{n..}$ (ただし、MはBa、Sr、Ca、Mg等のアルカリ土類金属およびZnからなる群から選ばれる1種または2種以上であり、RはLi、Na、Kのアルカリ金属イオンからなる群から選ばれる少なくとも1種以上であり、XはF、Cl、Br、Iからなる群から選ばれる少なくとも1種以上であり、M'はBまたはA1であり、共賦活剤LnはSc、Y、La、Ce、Pr、Nd、Sm、Gd、Tb、Dy、Ho、Er、Tm、Yb、Lu、Cr、Mn、Bi、Sn、In、Sb、As、Ti、Zr、Hf、P、Nb、Ta、V、Mo、Wの中から選ばれる少なくとも1種以上である。)で示され、a、b、c、d、y、zはそれぞれ $0 \leq a \leq 0.4$ 、 $0 \leq b \leq 0$ 、 $0 \leq c \leq 0$ 、 $0 \leq d \leq 0$ 、 $0 \leq y \leq 0$ 、 $0 \leq z \leq 0$ 。

1. $0 \leq c \leq 0.1$, $0 \leq d \leq 0.1$, $0.00001 \leq y \leq 0.1$, $0 \leq z \leq 0.3$ の範囲にある蓄光性蛍光体であり、請求項12に記載の発明は、254 nmの紫外線を照射した後の発光スペクトルにおいて、440 nm以下の波長の最大発光ピークを有する請求項11記載の蓄光性蛍光体である。

【0012】本発明の蓄光性蛍光体において、MO (Mはアルカリ土類金属又はZn) は単独でもホスト結晶になり得る必須成分である。本発明の蓄光性蛍光体は、EuまたはPbで賦活されており、残光輝度が高く残光時間が長く、優れた残光特性を発揮する。

【0013】また、本発明の蓄光性蛍光体において、MO (Mはアルカリ土類金属又はZn) はSiO₂と共にホストを構成することができる。Euで賦活され、SiO₂の含有量の比を表すaが $0 < a \leq 0.4$ の範囲の本発明の蓄光性蛍光体は、太陽光や昼白色蛍光灯などのなどの可視光で効率良く励起され、530 nmを越える波長の発光ピークを有する、視認性の良好な蓄光性蛍光体である。また、本発明の蓄光性蛍光体は、530 nmを越える波長の発光ピークを有することに加えて、440 nmを越えて530 nm以下の範囲に少なくとも一つ以上の発光ピークを有することができ、530 nmを越える発光ピーク波長の励起スペクトルにおいて400 nmを越えて450 nm以下の範囲に最大励起波長を有し、かつ、440 nmを越えて530 nm以下の発光ピーク波長の励起スペクトルにおいて300 nm以上400 nm以下の範囲に最大励起波長を有することができ。この場合、励起波長を変えることによって例えば黄色や青色の多様な残光色が得られる。これは、従来から知られるアルカリ土類硅酸塩には見られない発光特性である。aのより好ましい範囲は、 $0.00005 \leq a \leq 0.3$ である。

【0014】yは賦活剤EuまたはPbの濃度を示すもので、 $0.00001 \leq y \leq 0.1$ の範囲である。yが0.00001未満では光吸収が悪く、肉眼で認識できるほどの残光輝度が得られず、逆に0.1を越えると濃度消光を起こし、残光輝度が低下する。yの好ましい範囲は $0.00005 \leq y \leq 0.05$ である。

【0015】zは共賦活剤Ln (Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, Wの中から選ばれる少なくとも1種以上である。) の濃度を示すもので、 $0 \leq z \leq 0.3$ の範囲の量でのLnの添加は残光輝度の向上に効果があるが、0.3を超えるとかえって残光輝度が低下する。zの好ましい範囲は0.2以下であり、より好ましい範囲は0.05以下である。

【0016】アルカリ金属イオンの添加は残光輝度の向上に寄与する。その濃度bは、 $0.00001 < b \leq 0.1$

の範囲にあることが好ましく、 $0.00001 < b \leq 0.08$ の範囲であることがより好ましい。同様に、ハロゲンイオンの添加は残光輝度の向上に寄与する。その濃度cは、 $0.00001 < c \leq 0.1$ の範囲にあることが好ましく、 $0.00001 < c \leq 0.08$ の範囲であることがより好ましい。

【0017】硼酸またはアルミナは、ホスト組成に対する割合dが $0 \leq d \leq 0.1$ の範囲でフランクスとして添加することができる。dは、 $0.00001 < d \leq 0.1$ の範囲にあることが好ましく、残光特性の点で、 $d \leq 0.1$ の範囲にあることが好ましい。

【0018】

【発明の実施の形態】本発明の蓄光性蛍光体は以下の焼結法で合成することができる。まず、本発明の蓄光性蛍光体の原料として、酸化物、炭酸塩、硝酸塩、リン酸塩、水酸化物、ハロゲン化物等が用いられる。

【0019】上記原料を秤量し、十分に混合した後アルミナるつぼに入れて空気中、不活性ガスもしくは還元雰囲気で1100~1600°Cで1~10時間焼成する。組成によっては、得られた焼成物を粉碎し、もう一度同じ条件で焼成する方法を採用することも可能である。以下、本発明を具体的な実施例により説明するが、本発明はこれら実施例に限定されたものではない。

【0020】(実施例1) 最終組成がCaO : Eu_{0.05}になるように原料CaCO₃, Eu₂O₃を秤量・混合し、空気中で1350°Cで2時間焼成した後、目的の蓄光性蛍光体を得た。図1に254 nmの紫外線を5分間照射した後、1分間経過した時点の発光スペクトルを示す。595 nm付近に主ピークを持つ発光特性を有することがわかる。また、暗所で目視でオレンジ色の発光が1時間以上にわたって観察された。照射停止後の相対発光強度の変化は図2に示した通りである。図3にCaO : Eu₂O₃の励起停止後1分間経った時点での発光強度とEu₂O₃の濃度との関係を示す。上記の組成のCaOの代わりにSrOを使っても、ほぼ同じ結果が得られた。

【0021】(実施例2) 実施例1の組成にさらに0.3 mol% Na₂CO₃を添加し、同様な条件で蓄光性蛍光体を作製した。照射停止後1分経過した時点での発光強度を比べたところ、本実施例の発光強度は実施例1の1.5倍以上強くなったことが確認された。

【0022】(実施例3) 実施例1の組成にさらに0.2 mol% Li₂Cl₂を添加し、同様な条件で蓄光性蛍光体を作製した。照射停止後1分経過した時点での発光強度を比べたところ、本実施例の発光強度は実施例1の1.2倍以上強くなかったことが確認された。

【0023】(実施例4) 実施例1の組成にさらに1.5 mol% H₃BO₃を添加し、実施例1と同様な条件で蓄光性蛍光体を作製した。照射停止後1分経過した時点での発光強度を比べたところ、本実施例の発光強度は実施例1の2.2倍以上強くなかったことが確認された。

【0024】(実施例5)最終組成がSrO・0.18
SiO₂:Eu_{0.002};Dy_{0.001}になるように原料SrCO₃, SiO₂, Eu₂O₃, Dy₂O₃を秤量・混合し、還元雰囲気で1300°Cで2時間焼成して目的の蓄光性蛍光体を得た。図4に昼白色蛍光灯(FL20SSN/18-B)を5分間照射した後、1分間経過した時点の発光スペクトルを示す。465nmと575nm付近に二つのピークを持つ発光特性を有することがわかる。この二つの発光ピーク波長の励起スペクトルをそれぞれ図5(a)と(b)に示す。本蓄光性蛍光体は、発光ピーク波長465nmの励起スペクトルにおいて330nmに最大励起波長を有し、かつ、発光ピーク波長575nmの励起スペクトルにおいて415nmに最大励起波長を有していることが分かる。したがって、本蓄光性蛍光体は、励起波長を変えることによって多様な残光色を得ることができる。実際、例えば、400nmの光を照射した後、暗所で黄色の残光が確認され、320nmの光を照射した後、青色の残光が確認された。上記の組成のDy₂O₃の代わりにNd₂O₃を使っても、ほぼ同じ結果が得られた。また、SrOの一部をMgOもしくはBaOで置き換えて、同様な結果が得られた。

【0025】(実施例6)最終組成がSrO:Pb_{0.0005}になるように原料SrCO₃, PbOを秤量・混合し、空気中で1350°Cで2時間焼成した後、目的の*

*蓄光性蛍光体を得た。図6に254nmの紫外線を5分間照射した後、1分間経過した時点の発光スペクトルを示す。395nm付近に主ピークを持つ発光特性を有することがわかる。また、暗所で目視で紫色の発光が30分以上にわたって観察された。

【0026】

【発明の効果】以上、述べたように、本発明による蓄光性蛍光体は、化学的に安定で従来の酸化物蓄光性蛍光体に比べて、より多様な発光波長を有すると共に、長残光時間・高残光輝度を実現し、表示の多色化などに大きく寄与するものである。

【図面の簡単な説明】

【図1】実施例1の光励起停止1分を経過した後の発光スペクトルである。

【図2】実施例1の光励起停止後の発光強度の時間変化である。

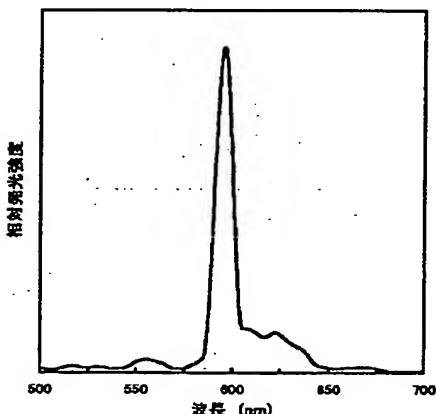
【図3】光励起停止1分を経過した後の発光強度とEu濃度と関係である。

【図4】実施例5の光励起停止1分を経過した後の発光スペクトルである。

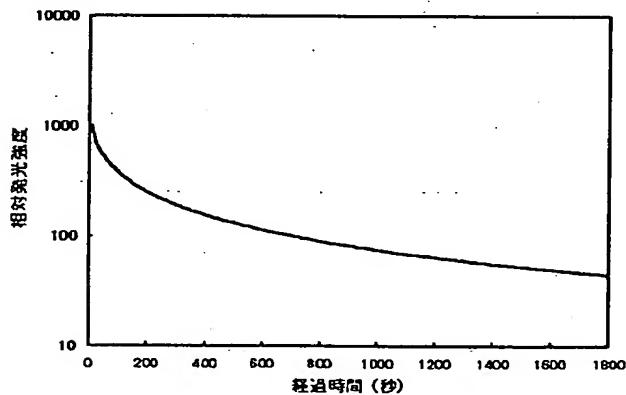
【図5】実施例5の励起スペクトルである。

【図6】実施例6の光励起停止1分を経過した後の発光スペクトルである。

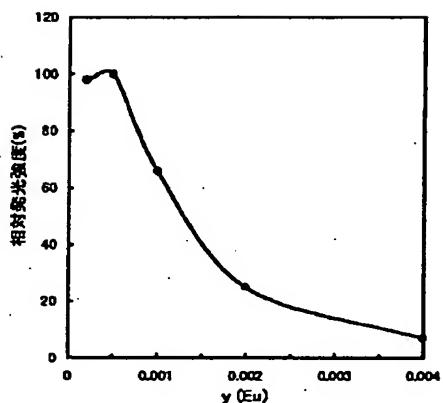
【図1】



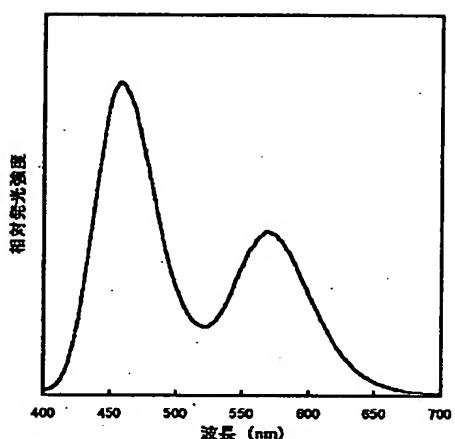
【図2】



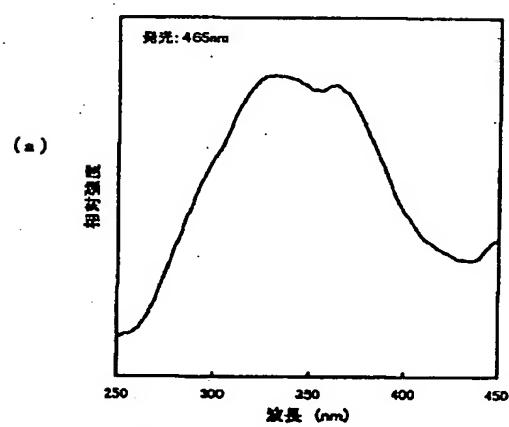
【図3】



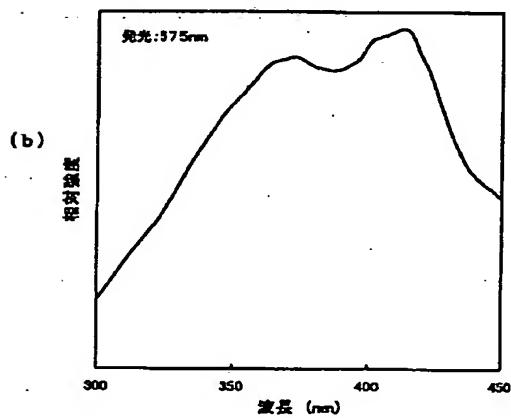
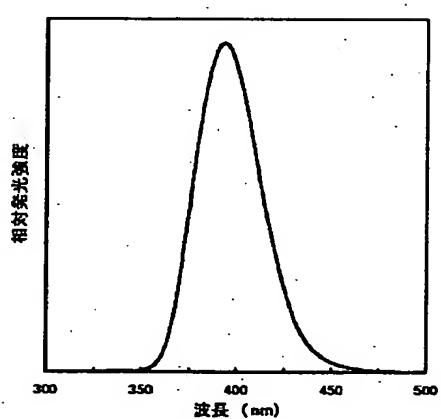
【図4】



【図5】



【図6】



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YA22 YA23 YA24 YA25 YA33
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(21)Application number : 11-119207 (71)Applicant : OHARA INC
 (22)Date of filing : 27.04.1999 (72)Inventor : FU KETSU
 OCHI YASUO

(54) PHOSPHORESCENT PHOSPHOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a phosphor having a high afterglow luminance and a long afterglow time by forming a phosphorescent phosphor having a specific Eu- activated or Pb- activated structure.

SOLUTION: The Eu-activated phosphorescent phosphor is represented by the formula: MO.aSiO₂.bR₂O.cX.dM'2O₃; Eu_yLn_z, is efficiently excited by the irradiation with visible light or an ultraviolet ray of 254 nm and has a luminescent peak at a wavelength of 530 nm or higher and a luminescent peak at a wavelength of 440–530 nm, The Pb-activated phosphorescent phosphor is represented by the formula: MO.aSiO₂.bR₂OcX.dM'2O₃; Pb_yLn_z, is excited by the irradiation with an ultraviolet ray of 254 nm and has the maximum peak at a wavelength of 440 nm or lower, In the formulas, M is Ba, Sr, Ca, Mg or Zn; R is Li, Na or K; X is F, Cl, Br or I; M' is B or Al; the coactivator Ln is Sc, Y, La, Ce, Pr, Nd, Ti, Zr, Hf or the like; 0≤a≤0.4; 0≤b≤0.1; 0≤c≤0.1; 0≤d≤0.1; 0.00001≤y≤0.1; and 0≤z≤0.3.

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CLAIMS

[Claim(s)]

[Claim 1] They are the phosphorescent materials by which activation was carried out by Eu. The chemical composition type $M_0 \cdot aSiO_2$ and $bR2 O \cdot cX \cdot dM_2O_3EuLnz$ (However, M is one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, or two sorts or more.) R is at least one or more sorts chosen from the group which consists of alkali-metal ion of Li, Na, and K. X is at least one or more sorts chosen from the group which consists of F, Cl, Br, and I. M' is B or aluminum. Coactivator Ln is at least one or more sorts chosen from Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, and W. They are the phosphorescent materials which are shown and a, b, c, d, y, and z have in the range of $0 < a \leq 0.4$, $0 < b \leq 0.1$, $0 < c \leq 0.1$, $0 < d \leq 0.1$, $0.00001 < y \leq 0.1$, and $0 < z \leq 0.3$, respectively.

[Claim 2] Phosphorescent materials according to claim 1 which have a in the range of $0 < a \leq 0.4$.
 [Claim 3] Phosphorescent materials according to claim 1 or 2 which are at least one or more sorts as which the aforementioned coactivator Ln is chosen from Nd, Dy, Tm, Mn, and Bi.
 [Claim 4] They are phosphorescent materials given in any 1 term among claims 1-3 which have b in the range of $0.00001 < b \leq 0.1$.
 [Claim 5] They are phosphorescent materials given in any 1 term among claims 1-4 which have c in the range of $0.00001 < c \leq 0.1$.
 [Claim 6] They are phosphorescent materials given in any 1 term among claims 1-5 which have d in the range of $0.00001 < d \leq 0.1$.

[Claim 7] They are phosphorescent materials given in any 1 term among claims 1-6 which have the luminescence peak of the wavelength exceeding 530nm in the emission spectrum after irradiating 254nm ultraviolet rays.

[Claim 8] They are phosphorescent materials given in any 1 term among claims 1-7 which have the luminescence peak of the wavelength exceeding 530nm in the emission spectrum after irradiating the light.

[Claim 9] having the luminescence peak of the wavelength exceeding 530nm in the emission spectrum after irradiating the light — in addition, the phosphorescent materials according to claim 8 which have another [more than] luminescence peak at least in the range of 530nm or less exceeding 440nm.

[Claim 10] It adds to having the luminescence peak of the wavelength exceeding 530nm in the emission spectrum after irradiating the light. They are the phosphorescent materials which have another [more than] luminescence peak at least in the range of 530nm or less exceeding 440nm. In the excitation spectrum of the emission peak wavelength exceeding 530nm, it has the maximum excitation wavelength in the range of 450nm or less exceeding 400nm. And phosphorescent materials which have the maximum excitation wavelength in the excitation spectrum of an emission peak wavelength 530nm or less exceeding 440nm in the 300nm or more range of 400nm or less.

[Claim 11] It is the phosphorescent materials by which activation was carried out by Pb, and the chemical composition type is $MO \cdot aSiO_2$ and $bR2 O \cdot cX \cdot dM_2O_3 : PbLnz$ (However, M is one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr,

calcium, and Mg, or two sorts or more.) R is at least one or more sorts chosen from the group which consists of alkali-metal ion of Li, Na, and K. X is at least one or more sorts chosen from the group which consists of F, Cl, Br, and I. M' is B or aluminum. Coactivator Ln is at least one or more sorts chosen from Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, and W. They are the phosphorescent materials which are shown and a, b, c, d, y, and z have in the range of $0 < a \leq 0.4$, $0 < b \leq 0.1$, $0 < c \leq 0.1$, $0 < d \leq 0.1$, $0.00001 < y \leq 0.1$, and $0 < z \leq 0.3$, respectively.

[Claim 12] Phosphorescent materials according to claim 11 which have the maximum luminescence peak with a wavelength of 440nm or less in the emission spectrum after irradiating 254nm ultraviolet rays.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the phosphorescent materials by which activation was carried out by Eu or Pb including alkaline earth metal or the oxide of Zn.

[0002]

[Description of the Prior Art] The phenomenon in which the matter emits the light near a visible range by the stimulus (excitation) from the outside with fluorescence — it is — a fluorescent lamp, a discharge lamp, and CRT (Cathode Ray Tube) — the so-called luminescence of the Braun tube etc. hits this. Although the matter which emits fluorescence is called fluorescent substance, the case where the fluorescence of the time amount (about 0.1s) of extent sensed for an eye after an excitation halt continues is called phosphorescence. And the fluorescent substance with high-persistence from which afterglow time amount reaches in several hours at a room temperature is called phosphorescent materials.

[0003] As such phosphorescent materials, sulfide systems, such as ZnSCu, (yellowish green luminescence), CaSr:Bi (blue luminescence), ZnCa:Cu (orange luminescence), and CaSr:Bi (purple luminescence), are known from ancient times. although current utilization be actually carried out only ZnSCu in order that chemistry endurance might be dramatically bad or might contain a poisonous thing like Cd, there be a trouble of be short in about t most 3 hours, afterglow time amount be decompose into the form of ZnSrH₂O->Zn+H₂S by the moisture in the ultraviolet rays further include in a daylight, and atmospheric air, the particle itself carry out melanism and it have the fatal fault that an afterglow brightness fall remarkably for a short period of time. Therefore, this luminous object was mainly limited to applications restricted dramatically, such as a watch with a luminous dial and an indoor night display.

[0004] Recently, phosphorescent materials are found out also for the oxide. For example, m(Sr_{1-x}Eu_x)O-nAl₂O₃ and 2OyB₃ system (China patent: CN1053807A) M_{1-x}Al₂O₄-xEu, and Dy system (publication number 8-127772), and m(Sr_{1-y}M₁a)O-n(Mg₁-bM₂b)O and a₂(Si₁-cGe_c)O₂:EuDy system are reported. Since afterglow brightness and afterglow time amount of both these ingredients improved substantially compared with the above mentioned sulfide system, a broader application is expected. However, the actual condition is that there is neither what has the luminescence peak of the wavelength which the maximum emission peak wavelength exceeds 440nm also in which system, and is in the range of 530nm or less, and exceeds >530nm, nor a thing which has the maximum luminescence peak with a wavelength of 440nm or less.

[0005]

[Problem(s) to be Solved by the Invention] This invention solves the trouble of the above-mentioned conventional technique, and makes it a technical problem to offer new oxide system phosphorescent materials with long afterglow time amount with high afterglow brightness.

[0006]

[Means for Solving the Problem] As a result of adding rare earth elements, Pb, etc. to the host presentation which is not known until now and doing test research wholeheartedly, this invention person does activation by Eu, finds out the phosphorescent materials which have the luminescence peak of the wavelength which exceeds 530nm in the emission spectrum after

irradiating 254nm ultraviolet rays, and does activation by Pb, finds out the phosphorescent materials which have the maximum luminescence peak with a wavelength of 440nm or less, and came to make this invention.

[0007] Namely, invention according to claim 1 is the phosphorescent materials by which activation was carried out by Eu. The chemical composition type MO-asiO₂ and bR2 O-cX-dM'2O3:EuYLnz (However, M is one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, or two sorts or more,) R is at least one or more sorts chosen from the group which consists of alkali-metal ion of Li, Na, and K, X is at least one or more sorts chosen from the group which consists of F, Cl, Br, and I. M' is B or aluminum. Coactivator Ln is at least one or more sorts chosen from Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, and W. It is shown and a, b, c, d, y, and z are 0<=a<=0.4, 0<=b<=0.1, 0<=c<=0.1, 0<=d<=0.1, 0.00001<y<=0.1, and the phosphorescent materials in the range of 0<=z<=0.3, respectively.

[0008] Invention according to claim 2 is phosphorescent materials according to claim 1 which have a in the range of 0< a<=0.4. Moreover, invention according to claim 3 The aforementioned coactivators Ln are the phosphorescent materials according to claim 1 or 2 which are at least one or more sorts chosen from Nd, Dy, Tm, Mn, and Bi. Invention according to claim 4 b is phosphorescent materials given in any 1 term among claims 1-3 in the range of 0.00001<b<=0.1. Invention according to claim 5 c is phosphorescent materials given in any 1 term among claims 1-4 in the range of 0.00001< c<=0.1. Invention according to claim 6 d is phosphorescent materials given in any 1 term among claims 1-5 in the range of 0.00001< d<=0.1. Invention according to claim 7 In the emission spectrum after irradiating 254nm ultraviolet rays, they are phosphorescent materials given in any 1 term among claims 1-8 which have the luminescence peak of the wavelength exceeding 530nm.

[0009] Moreover, invention according to claim 8 is set to the emission spectrum after irradiating the light. They are phosphorescent materials given in any 1 term among claims 1-7 which have the luminescence peak of the wavelength exceeding 530nm. Invention according to claim 9 having the luminescence peak of the wavelength exceeding 530nm in the emission spectrum after irradiating the light — in addition, they are the phosphorescent materials according to claim 8 which have another [more than] luminescence peak at least in the range of 530nm or less exceeding 530nm.

[0010] Moreover, invention according to claim 10 is set to the emission spectrum after irradiating the light. In addition, they are the phosphorescent materials which have another [more than] luminescence peak at least in the range of 530nm or less exceeding 440nm. having the maximum excitation wavelength exceeding 530nm — In the excitation spectrum of the emission peak wavelength exceeding 530nm, it has the maximum excitation wavelength in the range of 450nm or less exceeding 400nm. And they are the phosphorescent materials which have the maximum excitation wavelength in the excitation spectrum of an emission peak wavelength 530nm or less exceeding 440nm in the 300nm or more range of 400nm or less.

[0011] Moreover, invention according to claim 11 is the phosphorescent materials by which activation was carried out by Pb. The chemical composition type is MO-asiO₂ and bR2 O-cX-dM'2O3 :P byLnz (However, M is one sort chosen from the group which consists of alkaline earth metal and Zn, such as Ba, Sr, calcium, and Mg, or two sorts or more,) R is at least one or more sorts chosen from the group which consists of alkali-metal ion of Li, Na, and K, X is at least one or more sorts chosen from the group which consists of F, Cl, Br, and I. M' is B or aluminum. Coactivator Ln is at least one or more sorts chosen from Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, and W. It is shown and a, b, c, d, y, and z are 0<=a<=0.4, 0<=b<=0.1, 0<=c<=0.1, 0<=d<=0.1, 0.00001<y<=0.1, and the phosphorescent materials in the range of 0<=z<=0.3, respectively. Invention according to claim 12 is phosphorescent materials according to claim 11 which have the maximum luminescence peak with a wavelength of 440nm or less in the emission spectrum after irradiating 254nm ultraviolet rays.

[0012] In the phosphorescent materials of this invention, even when MO (M is alkaline earth metal or Zn) is independent, it is the indispensable component which can become a host crystal.

Activation of the phosphorescent materials of this invention is carried out by Eu or Pb, afterglow brightness is high, and its afterglow time amount is long, and they demonstrate the outstanding decay characteristic.

[0013] Moreover, in the phosphorescent materials of this invention, MO (M is alkaline earth metal or Zn) can constitute a host with SiO₂, a which activation is carried out by Eu and expresses the ratio of the content of SiO₂ — the phosphorescent materials of this invention of the range of $0 < \alpha \leq 0.4$ — sunlight, a daytime white fluorescent lamp, etc. — etc. — they are the

phosphorescent materials with good visibility which are efficiently excited by the light and have the luminescence peak of the wavelength exceeding 530nm. Moreover, the phosphorescent materials of this invention are added to having the luminescence peak of the wavelength exceeding 530nm. It can have another [more than] luminescence peak at least in the range of 530nm or less exceeding 440nm. In the excitation spectrum of the emission peak wavelength exceeding 530nm, it has the maximum excitation wavelength in the range of 450nm or less exceeding 400nm. And in the excitation spectrum of an emission peak wavelength 530nm or less, it can have the maximum excitation wavelength exceeding 440nm in the 300nm or more range of 400nm or less. In this case, yellow and various blue afterglow colors are obtained by changing excitation wavelength. This is a luminescence property which is not looked at by the alkaline earth silicate known from the former. The more desirable range of α is $0.00005 < \alpha \leq 0.3$.

[0014] y shows the concentration of Activators Eu or Pb, and the range of it is $0.00001 < y \leq 0.1$. y of optical absorption is bad at less than 0.00001, and afterglow brightness to the extent that it can recognize with the naked eye is not obtained, but if 0.1 is exceeded conversely, a lifting and afterglow brightness will fall concentration quenching. The desirable range of y is $0.00005 < y \leq 0.05$.

[0015] z Coactivator Ln (They are at least one or more sorts chosen from Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Cr, Mn, Bi, Sn, In, Sb, As, Ti, Zr, Hf, P, Nb, Ta, V, Mo, and W) Although concentration is shown and addition of Ln in the amount of the range of $0 < z \leq 0.3$ has effectiveness in improvement in afterglow brightness, if 0.3 is exceeded, afterglow brightness will fall on the contrary. The desirable range of z is 0.2 or less, and the more desirable range is 0.05 or less.

[0016] Addition of alkali-metal ion contributes to improvement in afterglow brightness. As for the concentration b, it is desirable that it is in the range of $0.00001 < b \leq 0.1$, and it is more desirable that it is the range of $0.00001 < b \leq 0.08$. Similarly, addition of halogen ion contributes to improvement in afterglow brightness. As for the concentration c, it is desirable that it is in the range of $0.00001 < c \leq 0.1$, and it is more desirable that it is the range of $0.00001 < c \leq 0.08$.

[0017] The rate d to a host presentation can add boric acid or an alumina as flux in $0 < d \leq 0.1$. As for d, it is desirable that it is in the range of $0.00001 < d$, it is the point of the decay characteristic and it is desirable that it is in the range of $d \leq 0.1$.

[0018] [Embodiment of the Invention] The phosphorescent materials of this invention are compoundable with the following sintering processes. First, an oxide, a carbonate, a nitrate, phosphate, a hydroxide, a halogenide, etc. are used as a raw material of the phosphorescent materials of this invention.

[0019] After carrying out weighing capacity of the above-mentioned raw material and fully mixing, it puts into an alumina crucible and calcinates at 1100–1600 degrees C in air gas or reducing atmosphere among air for 1 to 10 hours. It is also possible to adopt the approach of grinding the baking object obtained depending on the presentation, and calcinating on the same conditions once again. Hereafter, although the concrete example explained this invention, this invention was not limited to these examples.

[0020] (Example 1) Weighing capacity and after mixing and calcinating at 1350 degrees C in air for 2 hours, the target phosphorescent materials were obtained for raw materials Eu [CaCO₃ and] 2O₃, so that the last presentation might become CaO:Eu:0.001. After irradiating 254nm ultraviolet rays for 5 minutes at drawing 1, the emission spectrum at the time of passing for 1 minute is shown. It turns out that it has the luminescence property which has the main peak near 595nm. Moreover, orange luminescence was visually observed over 1 hours or more in the

dark place. Change of the relative luminescence reinforcement after an exposure halt is as having been shown in drawing 2. The relation between the luminescence reinforcement in the event of passing for 1 minute after an excitation halt of CaO:Eu in drawing 3 and the concentration of Eu is shown. Even if it used SrO instead of CaO of the above-mentioned presentation, the almost same result was obtained.

[0021] (Example 2) 0.3mol%Na₂CO₃ was added to the presentation of an example 1 at the pan, and phosphorescent materials were produced on the same conditions. When the luminescence reinforcement in the event of 1 minute passing after an exposure halt was measured, as for the luminescence reinforcement of this example, it was checked that the example 1 had become strong 1.5 or more times.

[0022] (Example 3) 0.2mol%LiCl was added to the presentation of an example 1 at the pan, and phosphorescent materials were produced on the same conditions. When the luminescence reinforcement in the event of 1 minute passing after an exposure halt was measured, as for the luminescence reinforcement of this example, it was checked that the example 1 had become strong 1.2 or more times.

[0023] (Example 4) 1.5mol%H₃BO₃ was added to the presentation of an example 1 at the pan, and phosphorescent materials were produced on the same conditions as an example 1. When the luminescence reinforcement in the event of 1 minute passing after an exposure halt was measured, as for the luminescence reinforcement of this example, it was checked that the example 1 had become strong 2.2 or more times.

[0024] (Example 5) It is a raw material SrCO₃ so that the last presentation may be set to SrO and 0.18SiO₂:Eu:0.0025Dy:0.005. Weighing capacity and mixing of SiO₂, Eu 2O₃ and Dy2O₃ were done, it calcinated at 1300 degrees C according to reducing atmosphere for 2 hours, and the target phosphorescent materials were obtained. After irradiating a daytime white fluorescent lamp (floor line 20SSN / 18-B) for 5 minutes at drawing 4, the emission spectrum at the time of passing for 1 minute is shown. It turns out that it has the luminescence property which has two peaks 485nm and near 575nm. The excitation spectrum of these two emission peak wavelengths is indicated to be drawing 5 (a) to (b), respectively. It turns out that these phosphorescent materials have the maximum excitation wavelength in 330nm in the excitation spectrum of 485nm of emission peak wavelengths, and it has the maximum excitation wavelength in 415nm in the excitation spectrum of 575nm of emission peak wavelengths. Therefore, these phosphorescent materials can obtain various afterglow colors by changing excitation wavelength. After irradiating 400nm light, yellow afterglow was checked in the dark place, and after irradiating the light which is 320nm, blue afterglow was actually checked. Even if it used Nd 2O₃ instead of Dy 2O₃ of the above-mentioned presentation, the almost same result was obtained. Moreover, the same result was obtained even if it replaced a part of SrO by MgO or BaO.

[0025] (Example 6) Weighing capacity and after mixing and calcinating at 1350 degrees C in air for 2 hours, the target phosphorescent materials were obtained for raw materials SrCO₃ and PbO, so that the last presentation might become Sr:Pr:0.00035. After irradiating 254nm ultraviolet rays for 5 minutes at drawing 6, the emission spectrum at the time of passing for 1 minute is shown. It turns out that it has the luminescence property which has the main peak near 395nm. Moreover, purple luminescence was visually observed over 30 minutes or more in the dark place.

[0026] [Effect of the Invention] As mentioned above, as stated, the phosphorescent materials by this invention realize long afterglow time amount and high afterglow brightness, and contribute to multiple colorization of a display etc. greatly while they have more variegated luminescence wavelength compared with the stable conventional oxide phosphorescent materials chemically.

[Translation done.]

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[0023] (Example 4) 1.5mol%H₃BO₃ was added to the presentation of an example 1 at the pan, and phosphorescent materials were produced on the same conditions as an example 1. When the luminescence reinforcement in the event of 1 minute passing after an exposure halt was measured, as for the luminescence reinforcement of this example, it was checked that the example 1 had become strong 2.2 or more times.

[0024] (Example 5) It is a raw material SrCO₃ so that the last presentation may be set to SrO and 0.18SiO₂:Eu:0.0025Dy:0.005. Weighing capacity and mixing of SiO₂, Eu 2O₃ and Dy2O₃ were done, it calcinated at 1300 degrees C according to reducing atmosphere for 2 hours, and the target phosphorescent materials were obtained. After irradiating a daytime white fluorescent lamp (floor line 20SSN / 18-B) for 5 minutes at drawing 4, the emission spectrum at the time of passing for 1 minute is shown. It turns out that it has the luminescence property which has two peaks 485nm and near 575nm. The excitation spectrum of these two emission peak wavelengths is indicated to be drawing 5 (a) to (b), respectively. It turns out that these phosphorescent materials have the maximum excitation wavelength in 330nm in the excitation spectrum of 485nm of emission peak wavelengths, and it has the maximum excitation wavelength in 415nm in the excitation spectrum of 575nm of emission peak wavelengths. Therefore, these phosphorescent materials can obtain various afterglow colors by changing excitation wavelength. After irradiating 400nm light, yellow afterglow was checked in the dark place, and after irradiating the light which is 320nm, blue afterglow was actually checked. Even if it used Nd 2O₃ instead of Dy 2O₃ of the above-mentioned presentation, the almost same result was obtained. Moreover, the same result was obtained even if it replaced a part of SrO by MgO or BaO.

[0025] (Example 6) Weighing capacity and after mixing and calcinating at 1350 degrees C in air for 2 hours, the target phosphorescent materials were obtained for raw materials SrCO₃ and PbO, so that the last presentation might become Sr:Pr:0.00035. After irradiating 254nm ultraviolet rays for 5 minutes at drawing 6, the emission spectrum at the time of passing for 1 minute is shown. It turns out that it has the luminescence property which has the main peak near 395nm. Moreover, purple luminescence was visually observed over 30 minutes or more in the dark place.

[0026] [Effect of the Invention] As mentioned above, as stated, the phosphorescent materials by this invention realize long afterglow time amount and high afterglow brightness, and contribute to multiple colorization of a display etc. greatly while they have more variegated luminescence wavelength compared with the stable conventional oxide phosphorescent materials chemically.

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the emission spectrum after optical-pumping half 1 minute of an example 1 passes.

[Drawing 2] It is time amount change of the luminescence reinforcement after an optical-pumping half of an example 1.

[Drawing 3] It is luminescence reinforcement, Eu concentration, and relation after optical-

pumping half 1 minute passes.

[Drawing 4] It is the emission spectrum after optical-pumping half 1 minute of an example 5 passes.

[Drawing 5] It is the excitation spectrum of an example 5.

[Drawing 6] It is the emission spectrum after optical-pumping half 1 minute of an example 6 passes.

[Translation done.]
